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ANTISEIZE AND ANTIWEAR ADDITIVES BASED ON DIETHERDITHIOPHOSPHORIC ACIDS DERIVED FROM ALKYL AND ARYL ESTERS OF GLYCERINE α-MONOCHLOROHYDRIN

by

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ABSTRACT *GLYCERINE α-MONOCHLOROHYDRIN

Dietherdithiophosphoric acids with the general formula $[ROCH_2(CHCl)CHO]_2PSSH$ are interacted with ethylene oxide and epichlorohydrin and the resultant compounds are tested as antiseize and antiwear additives in an attempt to develop organic compounds combining at least three active elements in a single molecule. Analysis of the products of interaction between dietherdithiophosphoric acids and ethylene oxide shows that they are very close in composition to trietherdithiophosphoric acids with formation by the equation

$$\left(\begin{matrix}ROCH_2\\ CH_2Cl\end{matrix}\!>\!CHO\right)_2 P\begin{matrix}\nearrow S\\ \searrow SH\end{matrix} + \underset{\diagdown O \diagup}{CH_2-CH_2} \rightarrow \left(\begin{matrix}ROCH_2\\ CH_2Cl\end{matrix}\!>\!CHO\right)_2 P\begin{matrix}\nearrow S\\ \searrow SCH_2-CH_2OH\end{matrix}$$

Physically, the β-hydroxyethyl esters obtained from the dietherdithiophosphoric acids studied are thick liquids with a weak yellowish tinge which dissolve well in organic solvents. The results for reaction with epichlorohydrin show compounds which are close in composition to trietherdithiophosphoric acids formed according to the equation

$$\left(\begin{matrix}ROCH_2\\ CH_2Cl\end{matrix}\!>\!CHO\right)_2 P\begin{matrix}\nearrow S\\ \searrow SH\end{matrix} + \underset{\diagdown O \diagup}{CH_2-CH}-CH_2Cl \rightarrow \left(\begin{matrix}ROCH_2\\ CH_2Cl\end{matrix}\!>\!CHO\right)_2 P\begin{matrix}\nearrow S\\ \searrow S\cdot CH_2\cdot CHOH\cdot CH_2Cl\end{matrix}$$

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The γ-chloro-β-hydroxypropyl esters of the dietherdithiophosphoric acids studied are viscous liquids with a weak yellowish tinge which dissolved readily in most organic solvents. The resultant trietherdithiophosphoric acids were tested as antiseize and antiwear additives in AK-15 oil on a four-ball tetrahedral friction machine with ShKh-6 steel balls (GOST 9490-60). The results show that both additives have high antiseize and antiwear properties with about equal numerical values for the generalized wear index. Tests of the anti-corrosion properties of the additives (GOST 8245-56) showed a reduction in the corrosiveness of AK-15 oil from 106 g/m^2 without the additives to 5-13 g/m^2 after introduction of the additives. Orig. art. has: 3 tables, 2 formulas.

ANTISIEZE AND ANTIWEAR ADDITIVES BASED ON DIETHERDITHIOPHOSPHORIC ACIDS DERIVED FROM ALKYL AND ARYL ESTERS OF GLYCERINE α-MONOCHLOROHYDRIN

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As we showed earlier [1], the reaction between alkyl and aryl esters of glycerin α-monochlorohydrin and phosporus pentasulfide occurs with formation of dietherdithiophosporic acids with the general formula $[ROCH_2(CH_2Cl)CHO]_2PSSH$. Zinc salts of these dietherdithiophosphoric acids are highly effective antisieze and antiwear additive for lubricating oils.

Continuing our research in the direction of obtaining organic compounds containing three and more active elements in one molecule we established as our goal the study of the reaction of the interaction of the cited dietherdithiophosphoric acids with ethylene oxide and epichlorohydrin and testing of the obtained compounds as antisieze and antiwear additives.

Addition of ethylene oxide to dietherdithiophosphoric acids [2] was carried out in a round-bottomed flask equipped with a mixer, reflux condenser, gas-feed tube, and thermometer.

In the flask, we mixed 0.06 mole of the investigated diether-dithiophosphoric acid with 50 ml of toluene. After this, about 0.09 mole of predried ethylene oxide, diluted with purified nitrogen, was slowly added to the solution at room temperature and with constant agitation. The reaction was accompanied by the liberation of a small amount of heat. The end of the reaction was established by the disappearance of the methyl orange acid reaction. Upon completion of the reaction, the product was freed from the solvent and analyzed. The results of the analysis (Table 1) showed that the obtained compounds are very close in composition to trietherdithiophosphoric acids formed according to the equation

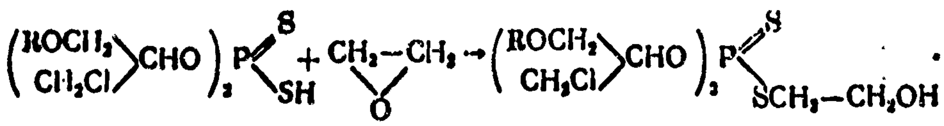

Table. 1. Characteristics of trietherdithiophosphoric acids of the type $[ROCH_2(CH_2Cl)CHO]_2PSSCH_2CH_2OH$.

R	Yield, %	d_4^{20}	p_D^{20}	Content, %					
				Phosphorus		Sulfur		Chlorine	
				Calc.	Found	Calc.	Found	Calc.	Found
CH_3	91,4	1,3295	1,5211	8,00	8,69	16,56	16,05	18,31	17,70
C_2H_5	91,6	1,2787	1,5150	7,46	8,12	15,44	14,81	17,07	16,42
$n-C_3H_7$	91,7	1,2208	1,5068	6,95	7,29	14,46	13,58	15,99	15,18
$n-C_4H_9$	92,3	1,2176	1,5043	6,57	6,93	13,60	13,02	15,01	14,35
$n-C_5H_{11}$	91,1	1,1975	1,5013	6,20	6,43	12,84	12,10	14,20	13,37
$n-C_6H_{13}$	92,1	1,1273	1,4829	5,87	5,59	12,15	11,36	13,44	12,69
C_6H_5	96,0	1,2868	1,5721	6,06	5,88	12,54	11,73	13,86	13,08
$p-CH_3C_6H_4$	95,7	1,2576	1,5665	5,74	5,58	11,89	11,18	13,14	12,46

The obtained β-hydroxyethyl esters of the investigated dietherdithiophosphoric acids are thick liquids with a weak yellow tinge. They dissolve well in organic solvents.

The reaction between dietherdithiophosphates and epichlorohydrin was conducted in the same instrument, but in place of the gas-feed tube a dropping funnel was installed. A sample of 0.06 mole of dietherdithiophosphoric acid and 50 ml toluene were placed in the flask. A solution of 0.06 mole epichlorohydrin in 10 ml toluene was added slowly to the mixture through the dropping

funnel. The reaction was accompanied by the liberation of heat, with the temperature of the reaction mixture increasing from room temperature to 33-34°. The mixture was heated on a water bath at a temperature of 60-70° for half an hour. The end of the reaction was determined by the absence of the methyl orange acid reaction.

Data from the analysis of the obtained products after distillation of the solvent (Table 2) show that they are very close in composition to the trietherdithiophosphoric acids formed according to the equation

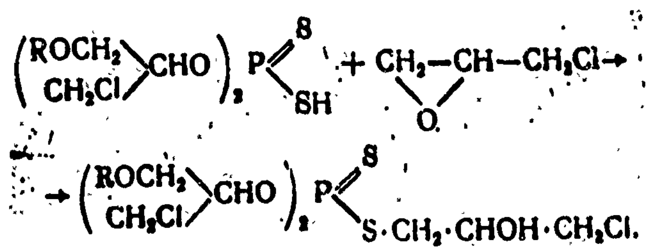

Table 2. Characteristics of trietherdithiophosphoric acids of the type $[ROCH_2(CH_2Cl)CHO]_2PSSCH_2{-}CHOH{-}CH_2Cl$.

R	Yield, %	d_4^{20}	n_D^{20}	Content, %: Phosphorus, Calc.	Phosphorus, Found	Sulfur, Calc.	Sulfur, Found	Chlorine, Calc.	Chlorine, Found
CH_3	86,0	1,3421	1,5249	7,11	7,25	14,71	14,05	24,40	23,34
C_2H_5	93,1	1,3029	1,5160	6,67	6.99	13,82	13,24	22,93	22,07
n-C_3H_7	93,6	1,2622	1,5109	6,30	6,54	13,03	13,67	21,62	20,85
n-C_4H_9	95,8	1,2496	1,5082	5,96	6,13	12,33	11,38	20,45	20,92
n-C_5H_{11}	91,2	1,2341	1,5058	5,65	6,05	11,70	11,14	19,41	18,47
n-C_6H_{13}	98,7	1,2016	1,5004	5,38	5,43	11,13	11,72	18,46	17,51
C_6H_5	97,3	1,3230	1,5731	5,53	5,48	11,45	10,81	19,00	19,68
p-$CH_3C_6H_4$	96,3	1,2816	1,5650	5,27	4,83	10,91	10,16	18,09	17,15

The γ-chlor-β-hydroxypropyl esters of the investigated dietherdithiophosphoric acids are viscous liquids with a weak yellow color. They dissolve readily in the majority of organic solvents.

The trietherdithiophosphoric acids shown in Tables 1 and 2 were tested in AK-15 oil as antisieze and antiwear additives. The generalized wear index (GWI) was determined on a four-ball friction machine with ShKh-6 balls (GOST 9490-60).

Comparison of the data in Tables 1 and 2 shows a clear distinction in the contents of sulfur, phosphorus, and chlorine. Thus, a molecule of additive of the type $[ROCH_2(CH_2Cl)CHO]_2PSSCH_2CH_2OH$ [A] contains 1.33 times as much chlorine and approximately 12% less phosphorus and sulfur than an additive of the type $[ROCH_2(CH_2Cl)CHO]_2PSSCH_2CHOHCH_2Cl$[B].

Table 3. Results of tests of AK-15 oil with trietherdithiophosphates.

R	A			B		
	Additive concentration, %	GWI	Corrosion, g/m^2	Additive concentration, %	GWI	Corrosion, g/m^2
C_2H_5	1,07	96,5	9,1	1,06	95,0	9,6
$n\text{-}C_3H_7$	1,14	100,7	8,8	1,13	92,3	10,8
$n\text{-}C_4H_9$	1,22	98,2	7,0	1,19	90,8	7,7
$n\text{-}C_5H_{11}$	1,29	94,5	8,7	1,25	93,7	12,2
$n\text{-}C_6H_{13}$	1,36	94,7	9,4	1,32	92,2	13,7
C_6H_5	1,32	96,3	9,9	1,28	95,3	4,3
$p\text{-}CH_3C_6H_4$	1,39	100,3	12,7	1,35	102,4	5,4
AK-15 oil without additive	—	23,0	106,0	—	—	—
Kleref-40	2,00	95,0	121,0	—	—	—

Despite this distinction, both additives possess high-antisieze and antiwear properties and are practically equal in the effectiveness of their action (Table 3).

The anticorrosion properties of the compounds prepared were determined according to GOST 8245-56. The results of the investigations (Table 3) showed that all of these coupounds have a strong anticorrosion effect; in their presence the corrosivity of AK-15 was reduced from 106 g/m^2 to 5-13 g/m^2.

Conclusions

1. It has been shown, that the condensation of dietherdithiophosphoric acids obtained from alkyl and aryl esters of glycerin α-monochlorhydrin with ethylene oxide and epichlorohydrin will produce the corresponding trietherdithiophosphoric acids.

2. It was established that the investigated trietherdithiophosphoric acids possess high antisieze, antiwear, and anticorrosion properties.

References

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